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(54) Liquid detergent compositions comprising coacervate mixture of alkylcellulose and carboxymethylcellulose and method for preparing them.

(57) Aqueous homogeneous liquid detergent compositions containing additive levels of alkylcellulose and carboxymethylcellulose and a mixture of anionic and nonionic surface-active agents are disclosed. The compositions have a pH in the neutral to mildly alkaline range. The alkylcellulose/carboxymethylcellulose is present as a coacervate capable of forming, in combination with the surfactants, a network of loosely associated droplets.

This network is tridimensional and provides means for stably and homogeneously suspending detergent components/additives which otherwise could not be incorporated, particularly ingredients which are substantially insoluble in the liquid compositions.

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LIQUID DETERGENT COMPOSITIONS COMPRISING  
COACERVATE MIXTURE OF ALKYLCELLULOSE AND CARBOXY-  
METHYLCELLULOSE AND METHOD FOR PREPARING THEM

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This invention relates to aqueous homogeneous liquid detergent compositions comprising surface-active agents and a mixture, in additive level, of alkylcellulose and carboxymethylcellulose. In more detail, the invention herein relates to concentrated homogeneous compositions comprising a coacervate mixture of known anti-redeposition agents in combination with high levels of anionic and nonionic surface-active agents. The mixture of anti-redeposition agents is present as a coacervate capable of forming, in combination with the surfactants, a network of loosely associated droplets. This tridimensional network provides means for stably and homogeneously suspending detergent components/additives which otherwise could not be incorporated, particularly ingredients which are substantially insoluble in the liquid matrix. The compositions herein are especially beneficial in several respects. First, the claimed compositions exhibit the benefits attached to the utilization of anti-redeposition agents. As of yet, it was virtually impossible to effectively incorporate the like agents in liquid detergent compositions.

Secondly, the tridimensional network provides a "honey comb-" or "wine cellar-"like structure, i.e., means for incorporating desirable detergent additives which up to now could not be compatibly incorporated into the like compositions because of phase separation, sedimentation, flocculation, coalescence or other known phenomena which can destabilize the like liquid compositions. In addition the compositions herein do not require highly viscous and/or thixotropic consistencies with a view to stabilize the cellulose ether coacervate.

The use of alkylcellulose and carboxymethylcellulose is well known in detergents and has found widespread commercial application, particularly in granular detergents, in an anti-redeposition functionality. However, it is also known that the incorporation of these cellulose ethers in liquid detergents is subject to considerable difficulties. The solubilization of anti-redeposition agents in liquid detergents is virtually impossible in presence of anionic surface-active agents. In general, it was tried to incorporate these agents via dispersion. However, stable cellulose ether dispersions require frequently high product viscosities with or without thixotropic properties. It is understood that product viscosity serves as a means to provide homogeneous dispersions as a result of decreased phase separation.

The prior art use of partial solubilization and/or dispersion techniques for incorporating cellulose ethers frequently aims at the incorporation of one cellulose ether species, i.e., anionic or nonionic.

Dispersion stability can allegedly also be obtained from using mixtures of anionic and nonionic cellulose ethers. This approach, in fact, aims at providing equilibrium between ascending and descending tendencies of the nonionic and anionic particles respectively. The latter approach is disclosed in German Patent Application 10 54 638 of April 9, 1959. Phosphate built, highly alkaline, liquid detergent compositions are disclosed containing mixtures of different cellulose ether derivatives. The '638 technology requires

an excess of methylcellulose over carboxymethylcellulose.

U.S. Patent 3.328.305, patented June 27, 1967, relates to a process for preparing detergent formulations containing separately prewetted cellulose ethers. The prewetting step is carried out with fatty acids which are liquid at ambient temperatures.

German Patent Application 24 02 225 discloses pourable, substantially non-aqueous, fluid masses having plastic Bingham-properties. Dispersed particulate solids are suspended in the fluid compositions with the aid of a fibrous tridimensional network. Fatty acid soaps constitute the network structure which network can serve to suspend particulate materials such as inorganic abrasives, or pigments.

Belgian Patent 758,553 and German Patent Application 19 55 556 also relate to suspending particulate materials in liquid detergents.

The prior art has, as of yet, not suggested means for effectively using mixtures of anionic and nonionic cellulose ethers, having a coacervate network structure, in liquid detergents. The art is non-suggestive of formulating stable liquid detergents containing cellulose ethers having a low viscosity without thixotropic properties. Moreover, the art is silent with respect to advantageously utilizing a cellulose ether coacervate network structure for stably incorporating ingredients which otherwise would be difficultly incorporatable, e.g., ingredients which are normally insoluble in the matrix.

The standing prior art prejudice against the possibility of effectively incorporating cellulose ethers, especially carboxymethylcellulose, into liquid detergents is based on general knowledge and supported by e.g. the disclosures of U.S. Patent 4.127.495 assigned to Hercules Inc. This prejudice is said to be particularly damaging towards using anionic surface-active agents in combination with cellulose ethers.

While the terms "coacervation" and "coacervate" are well-known in the technical community, for the sake of common

understanding these terms and the related term "coacervate network" can be described as follows.

The separation into two liquid phases in colloid systems is called coacervation. This separation results from a decrease in solubility of a lyophilic colloid. It leads to one colloid-rich and one colloid-poor phase.

A coacervate is in general an aggregate of colloidal droplets, held together by basic colloidal forces, frequently termed primary coacervate.

The term network herein stands for a coacervate network; it is a particular coacervate wherein colloidal isotropic droplets, having generally a diameter below 10 microns, are loosely associated into a three-dimensional network. The obtainment of a stable "tridimensional coacervate network" requires the presence of anionic and nonionic surface-active agents.

It is a major object of this invention to formulate homogeneous liquid detergent compositions containing additive levels of anti-redeposition agents.

It is a further object of this invention to provide concentrated homogeneous liquid detergents containing a mixture of anionic and nonionic cellulose ethers which compositions exhibit excellent storage stability over prolonged periods of time.

It is yet another object of this invention to formulate substantially phosphate builder-free concentrated neutral to mildly alkaline liquid detergent compositions containing stably incorporated therein detergent additives which additives up to now could not be used in liquid detergents.

The above and other advantages are now achieved with the aid of the composition and the method of this invention as described in more detail hereinafter.

#### SUMMARY OF THE INVENTION

This invention relates to aqueous homogeneous concentrated liquid detergents containing a coacervate of cellulose ethers

and a mixture of anionic and nonionic surface-active agents. The invention more specifically relates to homogeneous liquid detergent compositions containing :

- from 0.1% to 3% by weight of a coacervate of  $C_1$ - $C_4$  alkyl, possibly hydroxylated, cellulose (AC) and carboxymethyl-cellulose (CMC) in a weight ratio of CMC:AC of from 6:1 to 1:4;
- more than 20% by weight of a mixture of anionic and nonionic surface-active agents whereby the nonionic surfactant represents more than 3% by weight and whereby the weight ratio of anionic to nonionic is in the range from 1:1 to 8:1; and
- more than 10% by weight of water, whereby the weight ratio of the total ingredients to water is from 1:1 to 9:1.

Preferred compositions of this invention have a pH measured "as is" at 20°C of from 6.0-10. In another preferred aspect, the compositions herein comprise at least 5% by weight, calculated on the total detergent composition, of non-soap anionic surface-active agents.

The coacervate network provides storage stability and consequently an approach for beneficially utilizing the known anti-redeposition properties of the cellulose ethers in liquid detergents. Additionally, the tridimensional coacervate network can serve to stably incorporate all kinds of detergent additives which up to now could not be effectively incorporated into the like composition because of known incompatibility to the general liquid system.

The preferred alkylcellulose for use herein is methylcellulose.

Unless indicated to the contrary, the "%-indications" stand for --% by weight--.

#### DETAILED DESCRIPTION OF THE INVENTION

The compositions of this invention comprise as a first essential component from 0.1% to 3%, preferably from 0.5% to 1.5%, of a coacervate of a nonionic cellulose ether and an

anionic cellulose ether.

The nonionic cellulose ether is represented by a  $C_1-C_4$  alkyl, possibly hydroxylated, cellulose ether. Methylcellulose is the most preferred nonionic cellulose ether. The latter ingredient has normally a degree of substitution (DS) ranging from 0.5 to 2.8, preferably from 1.4 to 2.2. The nonionic cellulose ether is further characterized by a degree of polymerization (DP) between 50-1000, preferably between 150-300. Typical examples of suitable nonionic cellulose ethers for use herein include: methylcellulose DS 1.7; DP 200; ethylcellulose DS 1.5; DP 200; methylhydroxyethylcellulose DS 2.1; DP 200; and methylhydroxypropylcellulose DS 1.7; DP 200.

The DS indicates the number of substituted alkyl groups per anhydro-glucose unit. The DP expresses the number of anhydro-glucose units present in the polymer molecule.

The anionic cellulose ether is represented by carboxymethylcellulose having a DS ranging from 0.3 to 1.5, preferably from 0.6 to 0.9, and a DP in the range from 50-1000, preferably from 200-400. Carboxymethylcellulose is eminently well-known in the detergent art. The carboxymethylcellulose is preferably used as a salt with conventional cation such as sodium, potassium, amines, or substituted amines. A typical example of a suitable carboxymethylcellulose is the sodium salt having a DS of 0.7 and a DP of 250.

The weight ratio of the alkylcellulose to carboxymethylcellulose is normally in the range from 4:1 to 1:6, preferably from 1:1 to 1:3.

A second essential ingredient for use in the compositions herein is represented by a mixture of anionic and nonionic surface-active agents. This mixture is used in an amount of more than 20%, preferably in a level from 25% to 60%. The nonionic surface-active agent represents more than 3% (of the total detergent composition) whereas the weight ratio of anionic to nonionic surface-active agents is in the range from 1 to 1 to 8 to 1, preferably from 4:1 to 1:1. In a preferred embodiment, the non-soap anionic surface-active



agent shall represent at least 5%, preferably more than 8%, of the total detergent composition.

Suitable anionic surface-active agents are usually selected from the group of sulfonates, sulfates, and carboxylates/soaps. These anionic detergents are eminently well-known in the detergent arts and have found wide-spread commercial application. Preferred anionic water-soluble sulfonate or sulfate surfactants have in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms. Examples of preferred anionic surfactant are the reaction products obtained by sulfating  $C_8$ - $C_{18}$  fatty alcohols derived from tallow and coconut oil; alkylbenzene sulfonates wherein the alkyl group contains from about 8 to 15 carbon atoms; sodium alkylglyceryl ether sulfonates; ether sulfates of fatty alcohols derived from tallow and coconut oils; coconut fatty acid monoglyceride sulfates and sulfonates; and water-soluble salts of paraffin sulfonates having from about 8 to about 22 carbon atoms in the alkyl chain. Sulfonated olefin surfactants as more fully described in e.g. U.S. Patent Specification 3.332.880, incorporated herein by reference, can also be used. The neutralizing cation for the anionic synthetic sulfonates and/or sulfates is represented by conventional cations which are widely used in detergent technology such as sodium, potassium, amines and substituted amines.

A preferred anionic surfactant component herein is represented by the water-soluble salts of an alkylbenzene sulfonic acid having from about 10 to 13 carbon atoms in the alkyl group. Preferred are the sodium, potassium and substituted amine, such as triethanolamine, salts. Another preferred anionic surface-active agent is a sulfated  $C_{12}$ - $C_{14}$  fatty alcohol, possibly with a degree of ethoxylation in the range from 1-4, in combination with alkylbenzene sulfonates in a weight ratio of 3:1 to 1:3.

Still another preferred anionic surfactant is a paraffin sulfonate having from 12 to 20, preferably from 14 to 18 carbon atoms in the alkyl chain. The paraffin sulfonate can benefi-

cially be used in combination with  $C_{11}$ - $C_{13}$  alkylbenzene sulfonate in e.g. a weight ratio of 1:3 to 3:1.

The carboxylate surface-active agent is usually represented by the salts of fatty acids having from 10 to 24, preferably 12 to 18, carbon atoms. Suitable soap surface-active agents can originate from saturated and unsaturated fatty acids.

Examples of suitable saturated fatty acids for use in the compositions of this invention include capric, lauric, myristic, palmitic, stearic, arachadic and behenic acid. Suitable unsaturated fatty acid species include: palmitoleic, oleic, linoleic, linolenic and ricinoleic acid. Highly preferred for use herein are fatty acids having from 16 to 18 carbon atoms and which are comprised of at least 30% of unsaturated species. Other preferred fatty acids are represented by a mixture of saturated  $C_{10}$ - $C_{14}$  (coconut) fatty acids and oleic acid in a ratio (weight) of from 2:1 to 1:3.

The nonionic surface-active agents are frequently ethoxylated. All ethoxylated nonionic surfactants which are known to be suitable for use in detergent application can be used in the compositions of this invention. Examples of suitable nonionics include polyethoxylates derived from primary and secondary aliphatic alcohols having from 8 to about 24 carbon atoms, and having a HLB (hydrophilic-lipophilic balance) in the range from about 9 to 15. These ethoxylates frequently contain from 2 to about 14 moles of ethylene oxide per mole of hydrophobic moiety. The alkyl chain (hydrophobic moiety) can be represented by linear or branched fatty alcohols.

A preferred class of nonionic ethoxylates is represented by the condensation product of a fatty alcohol having from 12 to 15 carbon atoms and from about 4 to 10 moles of ethylene oxide per mole of fatty alcohol. Suitable species of this class of ethoxylates include: the condensation product of  $C_{12}$ - $C_{15}$  oxo-alcohols and 7 moles of ethylene oxide per mole of alcohol; the condensation product of narrow cut  $C_{14}$ - $C_{15}$  oxo-alcohols and 7 or 9 moles of ethylene oxide per mole of fatty (oxo) alcohol; the condensation product of a narrow cut  $C_{12}$ - $C_{13}$

fatty (oxo) alcohol and 6.5 moles of ethylene oxide per mole of fatty alcohol; and the condensation products of a  $C_{10}$ - $C_{14}$  coconut fatty alcohol with a degree of ethoxylation (moles EO/mole fatty alcohol) in the range from 5 to 8. The fatty oxo alcohols while mainly linear can have, depending upon the processing conditions and raw material olefins, a certain degree of branching, particularly short chain such as methyl branching. A degree of branching in the range from 15% to 50% (weight %) is frequently found in commercial oxo-alcohols.

Preferred nonionic ethoxylated components can also be represented by a mixture of 2 separately ethoxylated nonionic surfactants having a different degree of ethoxylation. For example, the nonionic ethoxylate can be represented by mixtures of a first ethoxylated surfactant containing from 3 to 7 moles of ethylene oxide per mole of hydrophobic moiety and a second ethoxylated species having from 8 to 14 moles of ethylene oxide per mole of hydrophobic moiety. A preferred nonionic ethoxylated mixture contains a lower ethoxylate which is the condensation product of a  $C_{12}$ - $C_{15}$  oxo-alcohol, with up to 50% (wt) branching, and from about 3 to 7 moles of ethylene oxide per mole of fatty oxo-alcohol, and a higher ethoxylate which is the condensation product of a  $C_{16}$ - $C_{19}$  oxo-alcohol with more than 50% (wt) branching and from about 8 to 14 moles of ethylene oxide per mole of branched oxo-alcohol.

The presence of nonionic and anionic surface-active agents is essential with a view to produce the coacervate network. It is believed that the anionic surfactant aids in the formation of a primary coacervate whereas the mixed non-soap anionic + nonionic surfactants promote the formation of a tridimensional network structure, usually starting from the primary coacervate.

The formation of the coacervate network can easily be ascertained e.g. by microscopic, particularly dark-field, examination of the composition. The network can be seen as a filamentous arrangement of aggregated droplets.

The coacervate network formation will occur provided water is used in a level in the range of from 10% to 50%. This formulation parameter is expressed in the weight ratio of the total ingredients to water as being in the range of from 1:1 to 9:1. The term "total ingredient" stands for the sum of all substances inclusive of surface-active agents, soaps, solvents, hydrotropes and organic and inorganic neutralizing agents.

The pH can have an adverse impact on the formation of the coacervate network. Under highly alkaline conditions e.g. pH above 10 the network formation can become more difficult, particularly if inorganic bases such as sodium or potassium hydroxide are used for pH adjustment. The use of organic bases, such as amines or substituted amines, is less damaging in this respect and some coacervate network formation can occur even under conditions of high alkalinity e.g. around pH 11.

The preferred compositions of this invention have a pH, measured "as is" and at 20°C, in the range from 6.0 to 10.

A preferred aspect of this invention relates to liquid detergent compositions which are essentially free of conventional water-soluble polyphosphate builders, having a pH in the range from 7 to 9 ("as is"-20°C). The term "water-soluble" qualifies the dissolution of the particular polyphosphate in the total liquid detergent. More than subadditive levels, e.g. above about 2%, of composition-soluble polyphosphates can inhibit the formation of the coacervate network because of excessive alkalinity and increase of ionic strength. It is understood that composition-insoluble polyphosphate salts can be stably incorporated with the aid of the wine cellar structure as explained hereinafter.

The compositions of this invention can be prepared by a variety of mixing techniques whereby the formation of the coacervate network can easily be ascertained. In a particularly simple and easy mixing sequence, the non-soap anionic surface-active agents are added, under mixing, to an aqueous

solution of the nonionic and anionic cellulose ethers, preferably at a temperature in the range from 15°C to 30°C. The resulting solution contains the primary coacervate droplets. The remainder of the anionic surfactants is thereafter added, under mixing, to the solution containing the primary coacervate. The nonionic surface-active agents are subsequently added under mixing. The pH of the solution throughout the mixing sequence shall be maintained above 6, usually in the range from 7 to 9. PH adjustments are made at the end of the sequence.

Solvents, pH regulating agents and other additives and optional ingredients can be added after the primary coacervate is formed or at the end of the mixing operation. - Conventional minor additives inclusive of dyes, perfumes, brighteners, can frequently be added at the end of the mixing process, i.e., after the addition of the nonionic surface-active agents.

The compositions of this invention can contain, in addition to the essential ingredients described hereinbefore, a series of conventional liquid detergent composition additives in the art established levels for their known functionality.

These conventional liquid detergent additives are, unless indicated differently, usually employed in levels below about 5%. Examples of the like additives which are well compatible with the claimed compositions include: enzymes, polyacids, suds regulants, opacifiers, anti-oxidants, bactericides, dyes, perfumes, brighteners, co-surfactants, photoactivators, incrustation inhibitors, corrosion inhibitors, enzyme-stabilizers, detergent builders and the like.

Detergent enzymes generally aid and augment the removal of specific stains. Suitable enzymes can be represented by proteases, amylases, lipases, glucose oxidases or mixtures thereof. Proteases and/or amylases are preferred in the claimed liquid concentrated compositions. They are frequently employed in a level from about 0.01% to about 1%. Mixtures of proteases and amylases can usually contain from 0.05% to 0.8% proteases and from 0.001% to 0.2% alpha-amylases.

Another preferred additive is represented by a polyacid or mixture of polyacids in an amount from about 0.05% to about 2%.

Preferred polyacid species for use herein can be represented by organo-phosphonic acids, particularly alkylene-polyamino-polyalkylene phosphonic acids such as ethylene diamine tetramethylenephosphonic acid, hexamethylene diamine-tetramethylenephosphonic acid, diethylene triaminepentamethylenephosphonic acid, and aminotrimethylenephosphonic acid or the salts thereof. These organophosphonic acids/salts are preferably used in an amount from 0.1%-0.8%. A non-phosphonated polyacid suitable for use include ethylenediaminetetraacetic acid and diethylene triamine pentaacetic acid.

The beneficial utilization of the claimed compositions under various usage conditions can require the utilization of a suds regulant. While generally all detergent suds regulants can be utilized preferred for use herein are alkylated polysiloxanes, such as dimethylpolysiloxane also frequently termed silicone, self emulsifiable silicones as e.g. known from German Patent Application DE-OS 26 46 057. The silicones are frequently used in a level not exceeding 0.5%, most preferably between 0.01% and 0.2%.

It can also be desirable to utilize opacifiers inasmuch as they contribute to create a uniform appearance of the concentrated liquid detergent compositions. Examples of suitable opacifiers include: polystyrene commercially known as LYTRON 621 manufactured by MONSANTO CHEMICAL CORPORATION. The opacifiers are frequently used in an amount from 0.3% to 1.5%.

The compositions herein can also contain conventional antioxidants for their known utility, frequently radical scavengers, in the art established levels i.e. 0.001% to 0.25% (by reference to total composition). These antioxidants can be introduced in conjunction with the fatty acid, especially the unsaturated fatty acid. While many suitable antioxidants are readily known and available for that purpose especially preferred for use in the compositions herein are: 2,6 ditertiary butyl-p-cresol, more commonly known as butylated



hydroxytoluene, BHT, and 2-tertiarybutyl-4-hydroxyanisole or 3-tertiarybutyl-4-hydroxyanisole more commonly known as BHA or butylated hydroxyanisole. Other suitable antioxidants are: 4,4'-thiobis(6-tert-butyl-m-cresol) and 2-methyl-4,6-dinonyl phenol.

In addition to the essential non-ionic/anionic surface-active mixture, the compositions herein can comprise additive levels, usually below 5%, of co-surface-active agents such as: nonionics other than ethoxylated species, zwitterionics, semipolar nonionics; and cationic surface-active agents. Examples of suitable semipolar nonionics include amine oxides, phosphine oxides and sulfoxides containing at least one  $C_{12}$ - $C_{14}$  alkyl group. Coconutalkyldimethyl amine oxide in a level of from 0.2 to 2% can be particularly useful inasmuch as, in addition to detergency, it can provide soil release properties. Cationic surfactants can also be utilized beneficially in the compositions herein, usually in a level in the range from 0.5% to 4%. Suitable cationic surfactant species include  $C_{10}$ - $C_{16}$  alkyl trimethylammonium salts.

The compositions herein can also contain as an optional ingredient from 0.0001% to 0.2% of a photoactivator. Suitable photoactivators are described in European Patent No. 0 026 744, granted May 5, 1982.

Suitable incrustation/decrustation inhibitors can be added to improve the appearance of used soiled textiles. They are frequently used in levels ranging from 0.5% to 2%. A well-known example of such a "crustation" inhibitor is a copolymer containing maleic acid and (meth)-acrylic acid monomers, as more fully described in European Patent Application 82.200602.9.

The compositions herein can also contain additive levels

(0.01%-0.3%) of particular aminosilanes with a view to improve machine compatibility, particularly in relation to enamel-coated surfaces. Suitable amino-silanes are disclosed in copending U.K. Patent Application 81-29069, filed on September 25, 1981.

Suitable enzyme stabilizers for use herein include short chain carboxylic acid, most preferably salts of formic acid, in levels of 0.1% to 3%, and subadditive levels of water-soluble Ca-salts. The utilization of these stabilizers is described in U.S. Patent 4.287.082 of September 1, 1981.

The claimed compositions can further contain composition-soluble detergent builders. Organic detergent, usually sequestering, builders are preferred although low levels of inorganic builders can be used provided they are soluble in the total detergent. Specific examples of suitable organic detergent builders include monomeric polycarboxylates such as citric acid; carboxymethyloxysuccinic acid; nitrilotriacetic alkali metal, salts thereof. Polymeric carboxylate builders inclusive of polyacrylate and polyhydroxyacrylate can also be used. The optional builder component can be used in the claimed compositions in levels from 2% to 10%.

Further, the claimed compositions can contain a series of useful detergent additives which could up to now not be used effectively in the like liquid detergent compositions because of insufficient storage stability, deactivation, flocculation, sedimentation and other phenomena which were known to adversely affect their effectiveness. The like additives are usually employed in levels of from 1% to 10%, preferably 2%-6%.

It is believed that these further additives can be stably incorporated with the aid of the tridimensional network obtained from the combined use of the nonionic and anionic cellulose ethers. This structure in fact resembles a fairly regular geometric arrangement of void spaces which can be filled up with marginally compatible, usually compo-



sition-insoluble ingredients. The network properties are such that the insoluble ingredients are kept within the void spaces without being subject to phase separation, frequently as a result of coagulation, sedimentation, creaming, etc.

Examples of ingredients which can be stably incorporated in the claimed compositions with the aid of the coacervate network include water-insoluble ingredients and composition-insoluble ingredients which have a non-negligible water-solubility. The terms "water-insoluble" and "composition-insoluble" as used herein stand for solubilities below 0.1% in water and the composition respectively. These ingredients shall have a particle size in the range from 1 micron to 100 microns, preferably from 1-20 microns. Water-insoluble ingredients can be represented by inorganic builders such as Zeolite A having the formula  $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12}\cdot 27\text{H}_2\text{O}$ ; Zeolite X :  $\text{Na}_{86}(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}\cdot 264\text{H}_2\text{O}$ ; and Zeolite P(B) :  $\text{Na}_6(\text{AlO}_2)_6(\text{SiO}_2)_{10}\cdot 15\text{H}_2\text{O}$ . These zeolites have frequently primary particle sizes of from 1-6 microns.

Other examples of insoluble additives are suds depressors such as hydrophobic silica, microcrystalline waxes, and fabric treatment/softening agents such as smectite clays.

Composition-insoluble ingredients can also include inorganic builders such as salts of pyrophosphates, anti-corrosion agents e.g. sodium aluminate, particularly upon use of this aluminate in neutral to mildly alkaline compositions, oxygen-bleach activators such as tetra-acetylene diamine (TAED), oxygen bleaches, e.g., the alkaline earth metal salts of perborates, antibactericides, immobilized enzymes and homopolymeric and copolymeric additives such as polycarboxylates having sequestrant and anti-redeposition functionalities.

Another class of composition-insoluble ingredients that can be stably incorporated herein includes coated, especially micro-encapsulated, additives such as enzymes, bactericidal agents, bleaches and activators therefore, perfumes, dyes, suds regulants anti-corrosion agents and more in general any kind of desirable additives which heretofore were not compa-

tible with concentrated liquid detergent compositions.

The following liquid detergents were prepared by mixing the individual ingredients in the listed proportions thereby using the method set forth in Claim 10.

INGREDIENT	COMPOSITIONS							
	Examples							
	A	I	II	III	IV	V	B	C
Carboxymethylcellulose(1)	1.0	1.0	0.7	0.5	0.7	0.7	0.7	0.7
Methylcellulose(2)	-	0.5	0.3	0.5	-	-	0.3	0.3
Methylhydroxyethylcellulose (3)	-	-	-	-	0.3	-	-	-
Methylhydroxypropylcellulose (4)	-	-	-	-	-	0.3	-	-
Linear dodecylbenzene sulfonate sodium salt	11	11	11	11	11	11	11	6
Condensation product of C13-C15 oxo alcohol & 7 moles of ethylene oxide per mole alcohol	12	12	12	12	12	12	-	6
Fatty acid (mixture of lauric & myristic acids in a weight ratio of about 3:1)	10	10	10	10	10	10	10	5
Oleic acid	5	5	5	5	5	5	5	3
Citric acid	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Diethylenetriamine pentamethylene phosphonic acid	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Alkaline protease(5)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Amylase (6)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Stilbene brightener	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Silicone emulsion(DB 110A ex Dow Corning)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Ethanol	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
1,2 Propanediol	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
Triethanolamine	5.0	5.0	5.0	5.0	5.0	5.0	5.0	2.0
Caustic	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.0
Coconut alcohol sulfate triethanolamine salt	4.0	4.0	4.0	4.0	4.0	4.0	4.0	2.0
Sodium formate	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CaCl <sub>2</sub> · 2H <sub>2</sub> O	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Water	35.0	35.5	35	35	35	35	47	72
Dyes, perfumes, opacifiers	b a l a n c e t o 100							
pH ("as is" - 20°C)	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
Brookfield viscosity in Cps at 25°C	75	250	180	250	120	130	280	150

- (1) Carboxymethylcellulose - TYLOSE<sup>®</sup> C30 - Supplied by HOECHST AG - DS : 0.64; DP : 250.
- (2) Methylcellulose - TYLOSE<sup>®</sup> MH20 - Supplied by HOECHST AG - DS : 1.75; DP : 200.
- (3) Methylhydroxyethylcellulose - WALOCEL<sup>®</sup> - Supplied by WOLFF WALSRODE - DS : 2.1; DP : 195.
- (4) Methylhydroxypropylcellulose - WALOCEL<sup>®</sup> - Supplied by WOLFF WALSRODE - DS : 1.7; DP : 190.
- (5) MAXATASE<sup>®</sup> supplied by GIST-BROCADES.
- (6) RAPIDASE<sup>®</sup> - Supplied by GIST-BROCADES.

These detergent compositions were evaluated, in parallel, for coacervate network formation, ascertained by microscopic examination, and storage stability (room temperature, 1 week) with the following results.

	COMPOSITIONS							
	A	Examples					B	C
		I	II	III	IV	V		
Coacervate network	no	yes	yes	yes	yes	yes	no	no
Storage stability	phase separation	homogeneous					phase separation	

The above results demonstrate the benefits derived from the compositions in accordance with this invention vs. closely related prior art compositions. The results highlight the claim criticalities --Composition A absence of AC; Composition B absence of nonionic ethoxylate; Composition C ratio total ingredients:water below 1:1.

Additional liquid compositions of this invention having the listed formulae were prepared thereby using the techniques of Examples I-V.

INGREDIENTS	VI	VII	VIII	IX	X	XI	XII
Carboxymethylcellulose	0.7	0.7	0.7	0.7	0.7	0.5	0.7
Methylcellulose	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Linear dodecylbenzenesulfonate sodium salt	5.0	5.0	6.0	6.0	12.0	15.0	-
Alpha-olefin sulfonate sodium salt	-	6.0	-	-	-	-	-
Paraffin sulfonate sodium salt	6.0	-	-	6.0	6.0	-	6.0
Coconutalkylsulfonate sodium salt	4.0	4.0	10.0	4.0	4.0	-	10.0
Condensation product of C13-C15 oxo-alcohol & 7 moles alcohol	10.0	12.0	10.0	12.0	20.0	15.0	12.0
C12-C14 trimethylammonium-chloride	2.0	1.5	2.0	-	-	-	-
3:1 mixture of lauric and myristic acids	10.0	10.0	10.0	10.0	-	10.0	10.0
Oleic acid	5.0	5.0	5.0	5.0	-	5.0	5.0
Citric acid	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Diethylenetriamine penta methylenephosphonic acid	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Ethanol	3.0	3.0	3.0	3.0	3.0	3.0	3.0
1,2 propanediol	8.0	10.0	6.0	8.0	15.0	3.0	3
Triethanolamine	3.0	3.0	7.0	3.0	2.0	2.0	5
Sodium hydroxide	1.4	1.5	1.0	1.5	≠	1.3	0.7
Potassium hydroxide	1.9	1.8	1.4	1.5	≠	1.5	1.4
Sodium formate	1.0	1.0	1.0	2.0	1.0	1.0	1.5
CaCl <sub>2</sub> ·2H <sub>2</sub> O	0.02	0.02	0.04	0.04	0.10	0.04	0.02
Protease	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Amylase	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Stilbene brightener	0.25	0.25	0.25	0.25	0.25	0.25	0.25
Silicone suds regulant	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water	36.0	32.0	33.0	35.0	33.0	39.0	39.0
Minors such as dyes, perfumes, opacifiers, etc.	b a l a n c e t o 100						
pH ("as is" - 20°C)	7.7	7.7	7.7	7.7	7.7	7.7	7.7
Brookfield viscosity in Cps at 25°C	100	100	70	130	60	120	100

The above compositions which contain the coacervate network exhibit excellent storage stability characteristics.

Additional liquid detergents were prepared having the compositions below.

<u>INGREDIENTS</u>	<u>COMPOSITIONS</u>	
	<u>EXAMPLE XIII</u>	<u>REFERENCE D</u>
Carboxymethylcellulose(1)	0.7	-
Methylcellulose(2)	0.4	-
Linear dodecylbenzene sulfo- nate sodium salt	11	11
Condensation product of C13- C15 oxo alcohol & 7 moles of ethylene oxide per mole alcohol	12	12
3:1 mixture of lauric and myristic acids	10	10
Oleic acid	5	5
Citric acid	0.2	0.2
Diethylenetriamine pentamethylene phosphonic acid	0.6	0.6
Protease(5)	0.05	0.05
Amylase(6)	0.3	0.3
Stilbene brightener	0.25	0.25
Silicone emulsion(DB110A ex Dow Corning)	0.20	0.20
Ethanol	3.00	3.00
1,2-Propanediol	9.00	9.00
Triethanolamine	5.00	5.00
Caustic	1.50	1.50
Coconut alcohol sulfate trietha- nolamine salt	4.00	4.00
Sodium formate	1.00	1.00
CaCl <sub>2</sub> , 2H <sub>2</sub> O	0.02	0.02
Water	35.0	36.0
Minors such as dyes, perfumes, opacifiers, etc.	balance to 100	
pH	7.7	7.7
Additives	See Listing	

(1), (2), (5), (6) - as defined in Examples I to V.

Additives

- (a) Hydrophobic silica: QUOSO WR50<sup>®</sup> from PHILADELPHIA QUARTZ Company - Particle size mean average: 5 microns.
- (b) Zeolite A :  $\text{Na}_{12}(\text{SiO}_2 \cdot \text{AlO}_2)_{12} \cdot 27\text{H}_2\text{O}$ ; particle size: 2-5 microns.
- (c) Silicone oil : polydimethylsiloxane - DB 100<sup>®</sup> supplied by DOW-CORNING - predispersed in nonionic surfactant with droplet size 50 microns.
- (d) Tetra-acetylenediamine: particle size mean of 60 microns.
- (e) Bentonite clay: particle size mean of 10 microns.
- (f) Sodium aluminate powder: supplied by DYNAMIT NOBEL, particle size: 50 microns.
- (g) Tetrapotassium pyrophosphate: particle size mean of about 70 microns.

Identical levels of the listed insoluble additives were added to Composition XIII of this invention, and to a substantially identical composition except that it did not contain the coacervate forming mixture of CMC and AC, termed Reference D. Stability readings (one week; room temperature) are summarized below.

ADDITIVES		COMPOSITIONS	
SPECIES	LEVEL	EXAMPLE XIII	REFERENCE D
Hydrophobic silica	2%	Homogeneous	Settling
Zeolite A	5%	Homogeneous	Sedimentation
Silicone oil	0.5%	Homogeneous	Floating
TAED	2%	Homogeneous	Settling
	5%	Homogeneous	Settling
Bentonite clay	5%	Homogeneous	Very rapid settling
Tetrapotassium pyrophosphate	5%	Homogeneous	Rapid settling

These comparative results confirm the unusual benefits derivable from the inventive compositions.

CLAIMS :

1. An aqueous, homogeneous liquid detergent composition containing surface-active agents, anti-redeposition agents, and optionally conventional ingredients for the like compositions, characterized in that it contains :
  - from 0.1% to 3% by weight of a coacervate of  $C_1$ - $C_4$  alkyl, possibly hydroxylated, cellulose(AC) and carboxymethyl-cellulose(CMC) in a weight ratio of CMC:AC of from 6:1 to 1:4;
  - more than 20% by weight of a mixture of anionic and nonionic surface-active agents whereby the nonionic surfactant represents more than 3% by weight and whereby the weight ratio of anionic to nonionic is in the range from 1:1 to 8:1; and
  - more than 10% by weight of water, whereby the weight ratio of the total ingredients to water is from 1:1 to 9:1.
2. The composition in accordance with Claim 1 wherein the weight ratio of CMC to AC is in the range from 3:1 to 1:1.
3. The composition in accordance with Claim 1 having a pH, measured "as is" at 20°C of from 6.0 to 10.
4. The composition in accordance with Claim 1 wherein the AC-CMC coacervate represents from 0.5% to 1.5% by weight.
5. The composition in accordance with Claim 1 wherein at least 5% by weight, calculated on the detergent composition, of the anionic surface-active agent is represented by a non-soap anionic surface-active agent.
6. The composition in accordance with Claim 1 wherein the ratio of the anionic to nonionic surface-active agents is in the ratio from 4:1 to 1:1.



7. The composition in accordance with Claim 1 wherein the mixture of anionic and nonionic surface-active agents represents from 25% to 60% by weight and wherein the nonionic surface-active agent is an ethoxylated nonionic having a hydrophilic-lipophilic balance (HLB) in the range from 9 to 15 and the non-soap anionic surface-active agent is a C<sub>10</sub>-C<sub>13</sub>-alkyl benzene sulfonate.

8. The composition in accordance with Claim 1 containing a tridimensional coacervate network and from 1% to 10% by weight of composition-insoluble detergent additives having a particle size in the range from 1 micron to 100 microns.

9. The composition in accordance with Claim 1 containing in addition:

- from 0.01% to 1% by weight of a mixture of proteases and alpha-amylases;
- from 0.05% to 2% by weight of a polyacid;
- up to 5% by weight of nonionic, semipolar nonionic and cationic co-surface-active agents; and
- from 0.1% to 3% by weight of formic acid salts.

10. A method for preparing the aqueous homogeneous liquid detergent in accordance with Claims 1, 5 and 8, comprising the following steps:

- adding the non-soap anionic surface-active agent to an aqueous solution of the mixture of cellulose ethers to thereby forming, under mixing, a primary coacervate; followed by
  - adding under mixing the remainder of the anionic surface-active agents; and subsequently
  - adding under mixing the nonionic surface-active agents to thereby form a coacervate network,
- with the further proviso during the mixing operations the pH is maintained above 6.0.

